



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>5</sup> :</b> <b>C08K 5/524, 5/5393, C08L 67/02</b> <b>C08L 69/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 91/17209</b> <b>(43) International Publication Date:</b> 14 November 1991 (14.11.91)
<b>(21) International Application Number:</b> PCT/US91/03067 <b>(22) International Filing Date:</b> 3 May 1991 (03.05.91) <b>(30) Priority data:</b> 520,690 7 May 1990 (07.05.90) US <b>(71) Applicant:</b> EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650 (US). <b>(72) Inventors:</b> CASSELL, Michael, Lynn ; 3714 Skyland Circle, Kingsport, TN 37664 (US). PRUETT, Wayne, Payton ; 101 Walton Court, Kingsport, TN 37663 (US). SMALL, James, Douglas, Jr. ; 780 Hamilton Road, Apartment D4, Blountville, TN 37617 (US). BRANSCOME, Larry, Wayne ; 407 Fieldpond Drive, Kingsport, TN 37664 (US).		<b>(74) Agent:</b> STEVENS, John, F.; 343 State Street, Rochester, NY 14650-2201 (US). <b>(81) Designated States:</b> AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> COPOLYESTERS OF TEREPHTHALIC ACID AND 1,4-CYCLOHEXANEDIMETHANOL HAVING IMPROVED MELT STABILITY <b>(57) Abstract</b> <p>Disclosed are copolyesters of terephthalic acid and 1,4-cyclohexanedimethanol containing selected phosphites or phosphonites which improve molecular weight retention after exposure to melt temperatures. In the phosphite or phosphonite, at least one of the P-O bonds is attached to an aryl radical. The compositions are useful in clear injection molding applications.</p>		

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COPOLYESTERS OF TEREPHTHALIC ACID AND  
1,4-CYCLOHEXANEDIMETHANOL HAVING  
IMPROVED MELT STABILITY

Technical Field

5           This invention relates to copolyesters of  
terephthalic acid and 1,4-cyclohexanedimethanol  
containing selected phosphites or phosphonites which  
improve molecular weight retention after exposure to  
melt temperatures. In the phosphite or phosphonite, at  
10       least one of the P-O bonds is attached to an aryl  
radical. The compositions are useful in clear injection  
molding applications.

Background of the Invention

15           Thermoplastic polyesters, such as poly(ethylene  
terephthalate) [PET], poly(butylene terephthalate)  
[PBT], and copolyesters of terephthalic acid and  
1,4-cyclohexanedimethanol [PCT] are useful as injection  
molding compounds for a variety of applications. These  
materials are sometimes reinforced with glass fibers or  
20       mineral fillers to enhance properties. However, with  
the present invention, clear injection molded articles  
are produced. Applications include automotive parts,  
appliance parts, and electrical-electronics parts. The  
thermoplastic polyesters have useful combinations of  
25       strength, heat resistance and chemical resistance for  
these uses.

30           Many times the thermoplastic polyester is processed  
into the final article of interest by injection molding.  
In the injection molding process, a quantity of material  
is melted but only a portion of it is injected into the  
mold. It is possible that melted material will remain  
in the molding machine for several minutes (perhaps as  
long as fifteen minutes) before it is injected and

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cooled. For this reason, it is desirable for the polymer to have excellent stability so that it will maintain high molecular weight even after several minutes holding time at melt temperatures. Maintaining  
5 high molecular weight is important in maintaining mechanical properties such as tensile, impact and flexural strengths.

This problem of melt stability is especially significant for PCT based materials because of their  
10 higher processing temperatures. The higher processing temperature accelerates the degradation rate.

A method has been discovered for maintaining the high inherent viscosity (I.V.) of the polymer by compounding certain stabilizers into the formulation.  
15 These stabilizers require that at least one of them be a phosphite or phosphonite, which will give the desired retention of inherent viscosity. Unexpectedly the stabilized copolyester composition requires little or no increase in injection pressure, at equivalent  
20 temperature and injection speed, in order to fill the mold. Also unexpected is the elimination of gate blush, and sprue sticking in the molding process of certain parts. One would expect that an effective stabilizer system would improve the retention of polyester I.V.,  
25 but it would also be expected that the increase in I.V. would be accompanied by a dramatic decrease in melt flow.

The use of certain phosphorous-based stabilizers in polycarbonate, and in polyester/polycarbonate systems,  
30 is disclosed in European Patent Applications 0 320 658 and 0 320 652, respectively.

European Patent Application 0 273 149 discloses the use of a phosphate compound as a component of a formulation. Phosphates are not within the scope of the  
35 present invention.

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Description of the Invention

According to the present invention there are provided clear copolyester molding compositions with improved stability in the melt comprising

- 5           a) a copolyester containing repeating units from terephthalic acid and 1,4-cyclohexane-dimethanol and having an inherent viscosity from 0.5 to 1.0,
- 10           b) 0.1-1.0%, preferably 0.25-0.5%, by weight of the total composition of an organic phosphite or phosphonite wherein at least one of the P-O bonds is attached to an aryl radical.

15           In a preferred embodiment of the present invention there is provided a molding composition with improved stability in the melt comprising

- 20           a) a copolyester having repeating units from a dicarboxylic acid component and a glycol component, at least 65 mol % of said acid component being terephthalic acid and at least 50 mol % of said glycol component being 1,4-cyclohexanedimethanol, said polyester having an inherent viscosity from 0.5 to 1.0, and
- 25           b) 0.1-1.0% by weight of the total composition of an organic phosphite or phosphonite wherein at least one of the P-O bonds is attached to an aryl radical.

30           The copolyesters of terephthalic acid and 1,4-cyclohexanedimethanol contains repeat units from a dicarboxylic acid component and a glycol component. The dicarboxylic acid component, a total of 100 mol %, is at least 65 mol % terephthalic acid and the glycol component, a total of 100 mol %, is at least 50 mol % 1,4-cyclohexanedimethanol.

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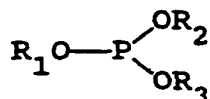
The dicarboxylic acid component may contain up to 35 mol % of other conventional aromatic, aliphatic or alicyclic dicarboxylic acids such as isophthalic acid, naphthalenedicarboxylic acid, cyclohexane-dicarboxylic acid, succinic acid, sebacic acid, adipic acid, glutaric acid, azelaic acid and the like. Isophthalic acid and cyclohexane dicarboxylic acid are preferred.

The glycol component may contain up to 50 mol % of other conventional aliphatic or alicyclic glycols such as diethylene glycol, triethylene glycol, ethylene glycol, propanediol, butanediol, pentanediol, hexanediol, 2,2,4,4-tetramethylcyclobutanediol, neopentyl glycol, and the like. Ethylene glycol is preferred.

The polyesters useful in this invention can be prepared by conventional polycondensation processes well known in the art. For example, the polyesters can be prepared by direct condensation of terephthalic acid or ester interchange using dimethyl terephthalate. The essential components of the polyester, e.g., terephthalic acid or dimethyl terephthalate and 1,4-cyclohexanedimethanol are commercially available.

The polyesters and copolyesters described above should have an I.V. (inherent viscosity) of from 0.5 to 1.0.

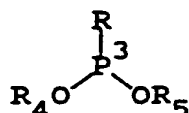
The phosphorous-based compound is either a phosphite or a phosphonite, wherein at least one of the P-O bonds is attached to an aryl radical. Such compounds may be represented by the formulas



Phosphite

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where at least one of  $R_1$ ,  $R_2$  and  $R_3$  is an aryl radical of 6 to 30 carbon atoms and any other(s) of  $R_1$ ,  $R_2$  and  $R_3$  are H or alkyl of 1 to 30 carbon atoms, or



Phosphonite

where at least one of  $R_3$ ,  $R_4$  and  $R_5$  is an aryl radical of 6 to 30 carbon atoms and any other(s)  $R_1$ ,  $R_2$  and  $R_3$  are H or alkyl of 1 to 30 carbon atoms.

Examples of such materials are Ultrinox 626 phosphite, Ultrinox 633 phosphite, (General Electric Chemicals), Irgafos 168 phosphite (Ciba-Geigy Corporation) and Sandostab P-EPQ phosphonite (Sandoz Chemicals).

In addition to the components discussed hereinabove, the blends of this invention may contain additives commonly employed with polyester resins, such as colorants, mold release agents, flame retardants, tougheners, plasticizers, ultraviolet light and heat stabilizers and the like.

The compositions of this invention are prepared by blending the components together by any convenient means to obtain an intimate blend. For example, the polyester can be mixed dry in any suitable blender or tumbler with the other components and the mixture melt-extruded. The extrudate can be chopped. The product is especially suitable as an injection molding material for producing molded articles.

The copolyester compositions described herein may be blended with other conventional polymers. If this is done, preferably the copoly ester compositions are blended with a polycarbonate. Useful polycarbonates are

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the polycarbonates of 4,4'-isopropylidenediphenol (bisphenol A). The I.V. of the polycarbonate is 0.3-1.2. The polycarbonate portion of the blends is prepared in the melt, in solution, or by interfacial polymerization techniques well known in the art.

Many such polycarbonates are commercially available, and are normally made by reacting bisphenol A with phosgene, dibutyl carbonate, diphenyl carbonate, etc.

The following examples are submitted for a better understanding of the invention.

In the examples, the following designations apply:

A - Irganox 1010 stabilizer, which is pentaerythrityl tetrakis(3,5-ditert-butyl-4-hydroxyphenylpropionate).

B - Weston 619 stabilizer, which is distearyl pentaerythrityldiphosphite.

C - Victastab HMP stabilizer, which is di(polyoxyethylene) hydroxymethyl phosphonate.

D - Ultrinox 633 stabilizer, which is bis(2,4,6-tri-t-butylphenyl)pentaerythritoldiphosphite.

E - Irgafos 168 stabilizer, which is tris(2,4-ditert-butylphenyl)phosphite.

#### Example 1

The copolyester in this example has repeat units from 100 mol % terephthalic acid, 65 mol % 1,4-cyclohexanedimethanol, and 35 mol % ethylene glycol.

Stabilizers are compounded into the copolyester at levels ranging from 0.1 to 0.6% by weight using a Brabender single screw extruder at 260-300°C. The pelletized samples are tested in a Tinius-Olsen melt indexer at temperatures ranging from 290°C to 305°C for up to 15 minutes. Inherent viscosity (I.V.) data is determined on samples taken at 5 minute intervals for



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15 minutes. Table 1 lists these samples with I.V. retention data.

#### Example 2

5 The copolyester in this example has repeat units from 100 mol % terephthalic acid, 80 mol % 1,4-cyclohexanedimethanol, and 20 mol % ethylene glycol.

10 Stabilizers are compounded into the copolyesters where the copolyesters contained different levels of acid and/or glycol moieties or an additional acid component. The samples are then tested on a Tinius-Olsen melt indexer at 300°C with samples being taken every 5 minutes for 15 minutes. Inherent viscosity data was determined, and is listed in Table 2 and 3.

#### Example 3

15 The copolyester in this example has repeat units from 95 mol % terephthalic acid, 5 mol % isophthalic acid, and 100 mol % 1,4-cyclohexanedimethanol.

20 A concentrate of Irgafos 168 (5 wt %) in the copolyester is compounded using a Werner-Pfleiderer ZSK-30 twin screw extruder at a temperature of 260°C. The concentrate is subsequently added to the copolyester, to yield an actual stabilizer concentration of 0.15 or 0.3 wt %, in a Reed 200TE injection molding machine hopper, and 5 x 5 x 0.0625 inch plaques are  
25 molded at equivalent injection rates and temperatures used to mold the copolyester. The copolyester I.V. before molding is 0.775 dl/g. The appropriate data appear in Table 4.

Table 1

<u>Example</u>	<u>Formulation</u>	<u>290°C</u>				<u>305°C</u>			
		<u>0 Min</u>	<u>5 Min</u>	<u>10 Min</u>	<u>15 Min</u>	<u>5 Min</u>	<u>10 Min</u>	<u>15 Min</u>	
1-1 (Control)	PCT (no additives)	0.733	0.684	0.640	0.620	0.621	0.572	0.509	
1-2	PCT + 0.1% A + 0.3% B	0.716	0.654	0.622	0.598	0.627	0.598	0.516	
1-3	PCT + 0.3% A + 0.6% B	0.658	0.625	0.584	0.566	0.587	0.528	0.486	
1-4	PCT + 0.3% C	0.720	0.660	0.624	0.596	0.616	0.552	0.502	
1-5	PCT + 0.6% C	0.716	0.626	0.610	0.581	0.583	0.532	0.471	
1-6	PCT + 0.1% A + 0.3% C	0.687	0.645	0.612	0.585	0.593	0.554	0.498	
1-7	PCT + 0.3% A + 0.6% C	0.729	0.657	0.625	0.603	0.621	0.565	0.529	
1-8	PCT + 0.1% A	0.733	0.697	0.675	0.663	0.662	0.594	0.540	
1-9	PCT + 0.3% D	0.730	0.715	0.683	0.672	0.685	0.595	0.595	!
1-10	PCT + 0.6% D	0.743	0.721	0.715	0.699	0.683	0.645	0.591	∞
1-11	PCT + 0.1% A + 0.3% D	0.735	0.720	0.695	0.674	0.670	0.629	0.551	!
1-12	PCT + 0.3% A + 0.3% D	0.739	0.732	0.712	0.709	0.686	0.642	0.620	
1-13	PCT + 0.3% E	0.768	0.697	0.677	0.641	0.664	0.616	0.559	
1-14	PCT + 0.6% E	0.747	0.705	0.683	0.649	0.658	0.605	0.532	
1-15	PCT + 0.1% A + 0.3% E	0.744	0.720	0.692	0.682	0.705	0.663	0.551	
1-16	PCT + 0.3% A + 0.6% E	0.729	0.709	0.684	0.664	0.652	0.623	0.550	

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TABLE 2

<u>Example</u>	<u>Formulation</u>	<u>300°C</u>			
		<u>0 Min</u>	<u>5 Min</u>	<u>10 Min</u>	<u>15 Min</u>
2-1 (Control)	PCT	0.726	0.620	0.596	0.539
2-2	PCT + 0.1% A	0.729	0.636	0.601	0.546
2-3	PCT + 0.3% B	0.676	0.606	0.571	0.536
2-4	PCT + 0.1% A + 0.3% B	0.702	0.623	0.581	0.579
2-5	PCT + 0.3% D	0.728	0.678	0.645	0.601
2-6	PCT + 0.1% A + 0.3% D	0.728	0.680	0.652	0.601

TABLE 3

<u>Example</u>	<u>Formulation</u>	<u>300°C</u>			
		<u>0 Min</u>	<u>5 Min</u>	<u>10 Min</u>	<u>15 Min</u>
2-7 (Control)	PCT	0.801	0.691	0.660	0.587
2-8	PCT + 0.1% A	0.822	0.753	0.695	0.644
2-9	PCT + 0.3% B	0.841	0.745	0.675	0.624
2-10	PCT + 0.1% A + 0.3% B	0.838	0.758	0.707	0.639
2-11	PCT + 0.3% D	0.830	0.745	0.698	0.641
2-12	PCT + 0.1% A + 0.3% D	0.832	0.777	0.716	0.665

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These examples show that the aromatic phosphite stabilizer (Ultranox 633) is superior to an aliphatic phosphite (Weston 619) for stabilizing copolyesters during melt processing. This product may be utilized in  
5 injection molded articles made using high molecular weight polymers with repeating units of terephthalic acid and 1,4-cyclohexanedimethanol.

Table 4PCT Formulations

<u>Example</u>	<u>Stabilizer Concentration (Wt %)</u>	<u>Temp (°C)</u>	<u>Injection Pressure, psi (kPa)</u>	<u>Hold Pressure, psi (kPa)</u>	<u>Injection Time (sec)</u>	<u>I.V. (dl/g)</u>	<u>Parts Stuck In Mold (%)</u>
3-1 (Control)	0	290	700 (4826)	600 (4137)	6.5	0.554	70
3-2	0.15	290	700 (4826)	600 (4137)	6.5	0.615	0
3-3 (Control)	0	290	600 (4137)	600 (4137)	6.0	0.555	100
3-4	0.30	290	600 (4137)	600 (4137)	6.0	0.593	0
3-5 (Control)	0	290	600 (4137)	600 (4137)	6.5	0.538	60
3-6	0.30	290	600 (4137)	600 (4137)	6.5	0.567	0

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The above examples demonstrate that, unexpectedly, only organic phosphites and phosphonites in which at least one of the P-O bonds is attached to an aryl radical are effective in providing a useful combination of melt stability and other desirable properties described herein.

Unless otherwise specified, all parts, percentages, ratios, etc., are by weight.

Inherent viscosity (I.V.) of the copolyester is measured at 25°C using 0.50 gram of polymer per 100 mL of a solvent consisting of 60 percent by weight phenol and 40 percent by weight tetrachloroethane.

While the invention has been described in detail with particular reference to preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

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Claims

1. A composition of matter characterized as consisting essentially of
  - a) a copolyester having repeat units from at least 65 mol % terephthalic acid and at least 50 mol % 1,4-cyclohexanedimethanol, said copolyester having an I.V. of 0.5-1.0, and
  - b) 0.1-1.0% by weight of the total composition of an organic phosphite or phosphonite wherein at least one of the P-O bonds thereof is attached to an aryl radical having 6-30 carbon atoms.
  
2. A composition of matter characterized as consisting essentially of
  - a) a copolyester having repeat units from at least 65 mol % terephthalic acid and at least 50 mol % 1,4-cyclohexanedimethanol, said copolyester having an I.V. of 0.5-1.0, and
  - b) 0.1-1.0% by weight of the total composition of an organic phosphite or phosphonite wherein at least one of the P-O bonds thereof is attached to an aryl radical having 6-30 carbon atoms, and
  - c) at least one additive selected from the group consisting of antioxidants, colorants, mold release agents, tougheners, nucleating agents, plasticizers, light stabilizers, heat stabilizers and flame retardants.
  
3. A clear, nonreinforced composition of matter characterized as comprising
  - a) a copolyester having repeat units from at least 65 mol % terephthalic acid and at least

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- 50 mol % 1,4-cyclohexanedimethanol, said  
copolyester having an I.V. of 0.5-1.0, and  
b) 0.1-1.0% by weight of the total composition of  
an organic phosphite or phosphonite wherein at  
least one of the P-O bonds thereof is attached  
to an aryl radical having 6-30 carbon atoms.
- 5
4. An injection molding composition characterized as  
comprising
- 10 a) 90-10 weight %, based on the weight of the  
composition, of the copolyester defined in  
Claim 1, and
- b) 10-90 weight %, based on the weight of the  
composition, of a polycarbonate.
- 15 c) 0.1-1.0% by weight of the total composition of  
an organic phosphite or phosphonite wherein at  
least one of the P-O bonds thereof is attached  
to an aryl radical having 6-30 carbon atoms.
5. The composition of Claim 1 wherein said polyester  
consists essentially of repeat units from a  
20 dicarboxylic acid component of 80-99% terephthalic  
acid and 20-1% isophthalic acid, and a glycol  
component of 1,4-cyclohexanedimethanol.
6. The composition of Claim 1 wherein said polyester  
consists essentially of repeat units from a  
25 dicarboxylic acid component of terephthalic acid  
and a glycol component characterized as consisting  
essentially of 60-95% 1,4-cyclohexanedimethanol and  
5-40% ethylene glycol.



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7. An injection molding composition characterized as comprising

5 a) 90-10 weight %, based on the weight of the composition, of the copolyester defined in Claim 2, and

b) 10-90 weight %, based on the weight of the composition, of a polycarbonate.

10 c) 0.1-1.0% by weight of the total composition of an organic phosphite or phosphonite wherein at least one of the P-O bonds thereof is attached to an aryl radical having 6-30 carbon atoms, and

15 d) at least one additive selected from the group consisting of antioxidants, colorants, mold release agents, tougheners, nucleating agents, plasticizers, light stabilizers, heat stabilizers and flame retardants.

8. The composition of Claim 3 wherein any acid component other than terephthalic acid is  
20 isophthalic acid, and any glycol component other than 1,4-cyclohexanedimethanol is ethylene glycol.

9. The composition of Claim 3 wherein any acid component other than terephthalic acid is 1,4-cyclohexanedicarboxylic acid.

## INTERNATIONAL SEARCH REPORT

International Applicati

PCT/US 91/03067

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and		
Int.C1.5	C 08 K 5/524	C 08 K 5/5393 C 08 L 67/02
C 08 L 69/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.C1.5	C 08 K	C 08 L
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
P,X	WO,A,9105820 (EASTMAN KODAK CO.) 2 May 1991, see claims ---	1-3, 5, 6 , 8, 9
X	RESEARCH DISCLOSURE, no. 313, May 1990, (Emsworth, GB), Anonymous: "Oriented polyester film", page 368, see abstract ---	1
X	EP,A,0005447 (CIBA-GEIGY AG) 28 November 1979, see page 7, line s 9-20; claims -----	1
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
20-08-1991	23 SEP 1991	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	MISS T. TAZELAAR	

Form PCT/ISA/210 (second sheet) (January 1985)

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9103067  
SA 47615

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 17/09/91  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A- 9105820	02-05-91	None	
EP-A- 0005447	28-11-79	JP-C- 1471975	27-12-88
		JP-A- 54141753	05-11-79
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		US-A- 4406842	27-09-83

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